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SOLUBILITIES OF DISOLVED GASES IN SEA WATER,

FINAL TECHNICAL REPORT

Contract N00014-78-C-0198

Office of Naval Research

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This final technical report is composed of two reprints plus the following summary of those two papers and a discussion of other work that is now in preparation for publication.

1. Oxygen: It was noted in the original proposal (p. 6) that "we make corrections to the fugacity for gas-gas and gas-water interactions in the vapor phase." Corrections for molecular interactions in a pure gas can be made from a knowledge of the virial coefficients for the gas. The presence of water vapor, however, complicates the problem, especially at higher temperatures, where the vapor pressure of water becomes larger. In the absence of experimental knowledge about gas-water interactions, we were using theoretical calculations to estimate the effect of the interaction. After it was found that the theoretical methods did not provide corrections to the solubility data with sufficient accuracy, we finally decided to adopt the direct empirical approach described in the attached reprint from Vol. 8, No. 9 (Benson, Krause and Peterson, 1979) of the Journal of Solution Chemistry. Although additional time is required to carry out the measurements from which the effect of the total pressure is determined, the results for the Henry coefficient are unequivocal and fully corrected.

The precision of the measurements of the solubility of oxygen (random error less than 0.02%) is an order of magnitude better than previous measurements on any gas over a significant

temperature range, and tests and comparison with other work indicate that systematic errors probably are negligible. Furthermore the accuracy of the measurements has made it possible to show that the expression

$$\ln k = a_0 + a_1/T + a_2/T^2$$

is a much better way to express the variation of solubility with temperature than the relationships previously used. Mass spectrometric measurements of the isotopic fractionation of $^{34}O_2/^{32}O_2$ during solution have provided the first quantitative determination of the variation of the fractionation with temperature, and have made possible an estimation of the size of the cavity occupied by the oxygen molecule in the water.

A second manuscript, "The concentration and isotopic fractionation of gases dissolved in freshwater in equilibrium with the atmosphere: 1. Oxygen," has been published in "Limnology and Oceanography" (Benson and Krause, 1980). A copy is included here. In it we have discussed how to obtain accurate values for the concentration of an atmospheric gas in water in equilibrium with air, including corrections for molecular interactions in the vapor phase. The results for oxygen show that the UNESCO tables for the solubility of oxygen give values in freshwater that are low by from 0.15% to 0.35% depending upon temperature.

2. <u>Hydrogen</u>: We have carried out several sets of determinations of the solubility of hydrogen. The results give very accurate values for oceanographic and limnological work, and they are especially significant because of the information they provide about the properties of liquid water.

A) <u>Pure Water</u>: Fig. 1 shows the results of our measurements on hydrogen in distilled water from 0 to 60°C. The clusters of solid circles at 0, 15, 35 and 55°C are drawn to indicate that measurements at several pressures were made, from which the corrections for molecular interactions in the vapor phase were obtained. (All points really lie essentially on the line at the same temperature.) Although the virial coefficients for pure hydrogen show that it is a "repulsive gas," the hydrogen-water vapor system behaves very nearly like an ideal gas. In fact, the variation of λ with t (°C) is given by

$$\lambda = 0.000345 - 1.83 \times 10^{-5}t,$$

which shows that below approximately room temperature it is a slightly "attractive gas," but it becomes "repulsive" above room temperature. Comparison with Eq. 21 in Benson, Krause and Peterson (1979) shows that relative to oxygen the vapor phase correction is smaller and varies less rapidly with temperature. Again, our function

CROZIER & YAMAMOTO
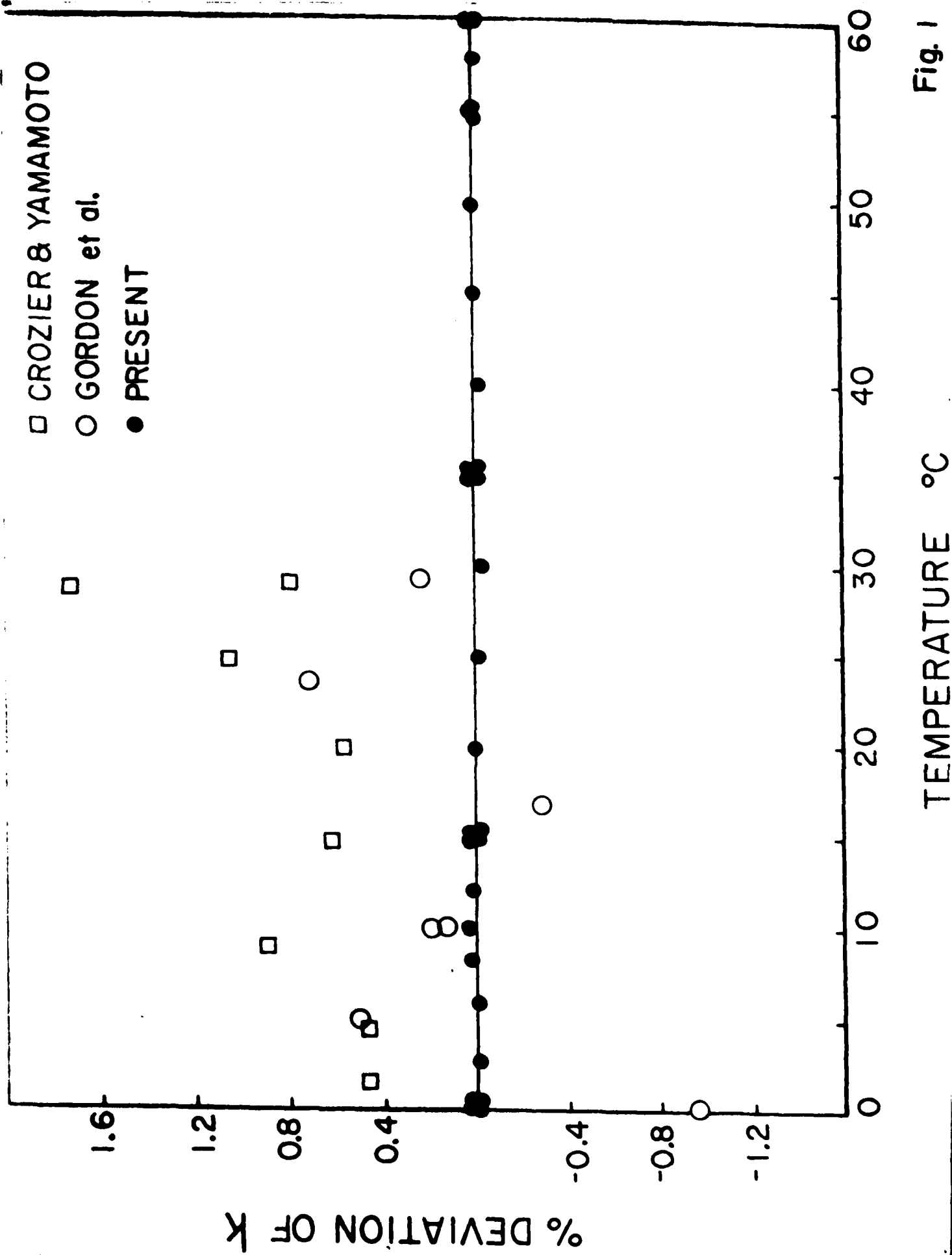GORDON et al.
PRESENT

% DEVIATION OF K

TEMPERATURE °C

Fig. 1

$$\ln k = a_0 + a_1/T + a_2/T^2$$

provides an excellent fit for the data. The standard
deviation for all the pure water measurements from 0
to 60°C is 0.016%. Fig. 1 also shows the experimental
results of Crozier and Yamamoto (1974) and Gordon et al.
(1977). The large scatter of their data is evident,
together with systematic deviations from our results.
Note that the ordinate axis has been compressed by a
factor of two compared to Fig. 4 in BKP for oxygen, in
order to keep the hydrogen points on the graph. It is
possible to calculate the thermodynamic function changes
for the solution of hydrogen in water, as we have done
for oxygen, but these will not be discussed here.

B) Seawater: Although it is well known that gas solubilities
decrease with increasing salinity (the "salting-out" effect),
the functional dependence of solubility on S has been
difficult to determine because very accurate measurements
are required. Carpenter (1966) found a non-linear
variation for the solubility of O_2 with chlorinity, and
he used a quadratic relationship. Green and Carritt (1967)
reported a series of measurements on oxygen to obtain the
ratio of the solubility in seawater to that in pure water.
The design of the experiment made potential systematic
errors in the individual solubility determinations tend
to cancel in the ratio. Green and Carritt showed that

within the limits of their measurements the Setschenow
relationship correctly describes the dependence of the
oxygen ratio on chlorinity. Furthermore, their results
provided the first reasonably accurate determination of
the way the salting-out coefficient varies with temperature.

We have measured the dependence of solubility on
salinity up to approximately 50‰ at 0, 10, 20 and 35°C.
The results are shown in Fig. 2 where it is clear that
ln (k_s/k_o) is extremely linear with salinity. (Fits to
salinity and chlorinity are equally good.) Although the
straight lines in Fig. 2 suggest that the Setschenow
equation fits the results very well, the tightness of fit
does not really become apparent until it is recognized
that the precision of the measurements is such that even
the slopes of the four lines are known with great accuracy
(0°C: 0.46%, 10°C: 0.12%, 20°C: 0.15%, 35°C: 0.04%).
In other words, these very accurate new results for
hydrogen not only verify the applicability of the
Setschenow relationship to hydrogen in seawater, but also
now make it possible to determine the functional dependence
of the salting-out coefficient upon temperature.   This
is illustrated in Fig. 3 where the salting-out coefficient
is plotted vs. 1/T.   (Error bars are shown on the solid
circle at 0°C, but the errors for the other three points
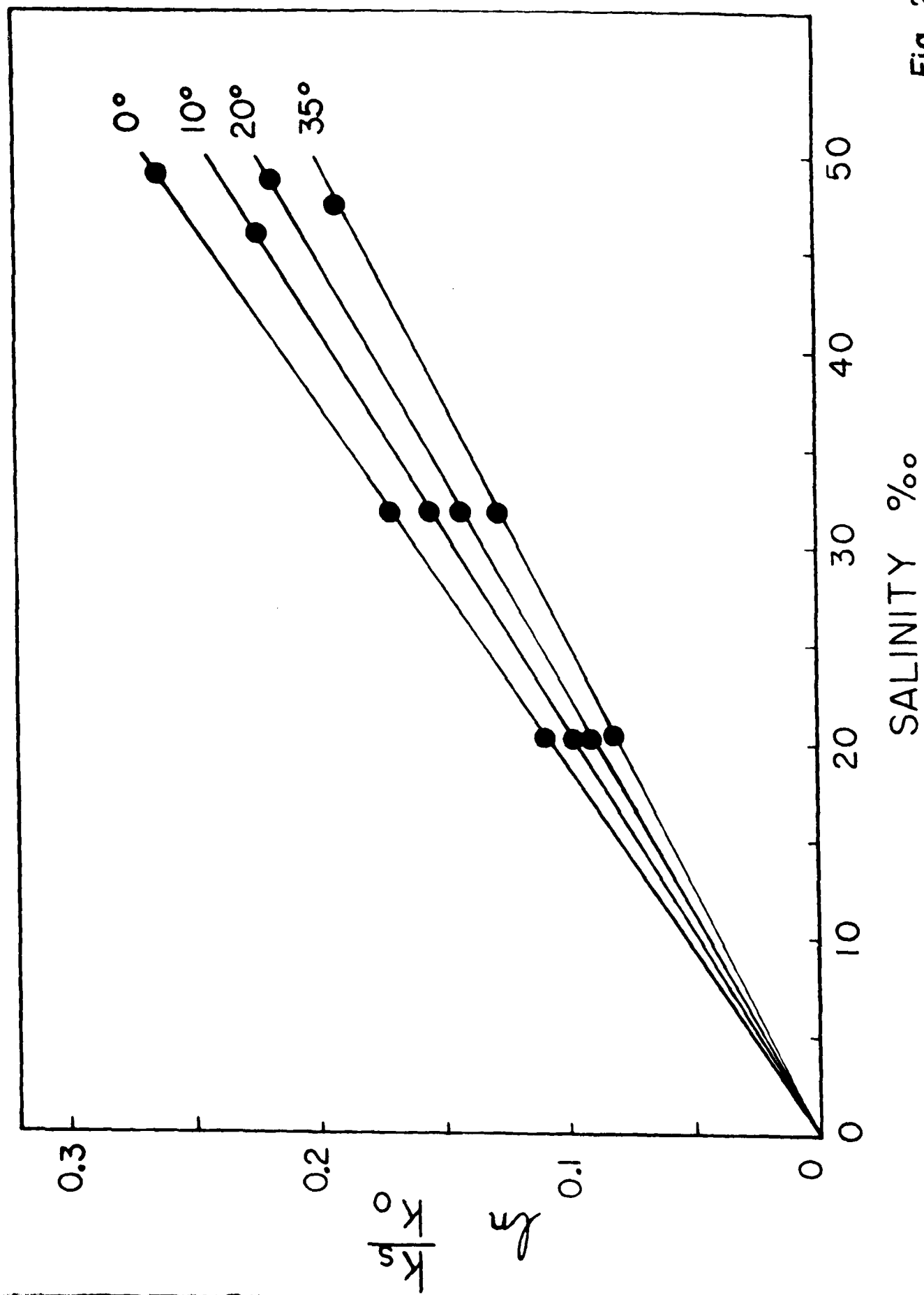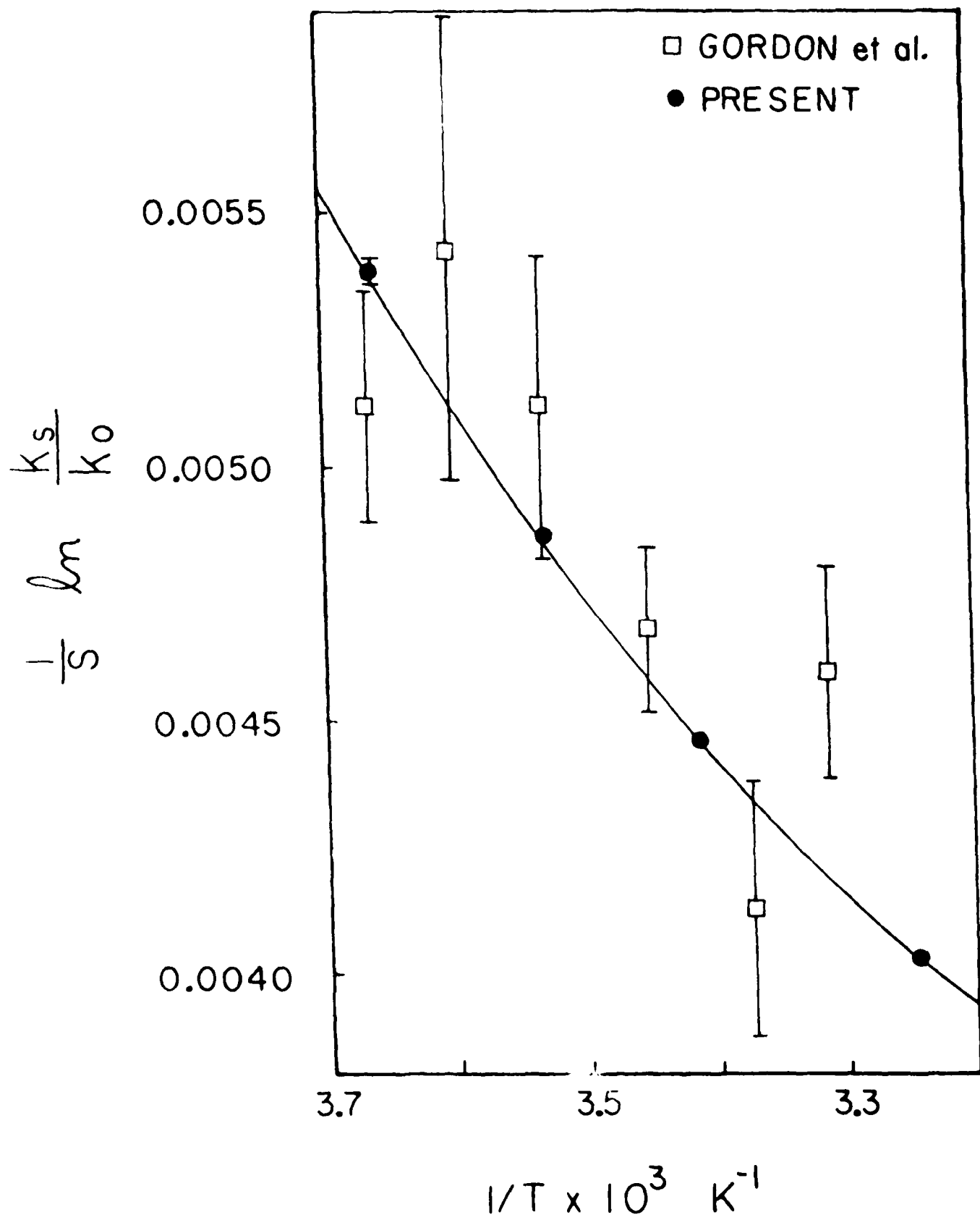are less than the size of the circles.)   It is clear that

Fig. 2

SALINITY ‰

$\ln \dfrac{k_s}{k_o}$

0°
10°
20°
35°

Fig. 3

the points lie on a smooth curve, and - like ln k - it is parabolic in 1/T. The open squares representing the results of Gordon et al. are generally consistent with our values, although, of course, their much larger errors and scatter preclude determination of the temperature dependence with any certainty.

Our final equation for the variation of the Henry coefficient with both temperature and salinity is

$$\ln k = 4.13352 + 4672.47/T - 768235/T^2$$
$$+ S(0.026112 - 15.684/T + 2737.0/T^2).$$

The salting-out coefficient in the parenthesis has its minimum at a temperature not very different from that for the solubility in pure water. The equation used by Green and Carritt for the Bunsen coefficient of oxygen was of the form

$$\ln \beta = A + B/T + C \ln T + DT$$
$$+ C\ell(A' + B'/T + C'\ln T + D'T).$$

Gordon et al. fitted their hydrogen data together with those of Crozier and Yamamoto, to the following function

$$\ln \beta = A + B/T + C \ln T$$
$$+ S(A' + B'T + C'T^2).$$

The fit of all our data (for both pure water and seawater) to our function is shown in Fig. 4. There were, of course,
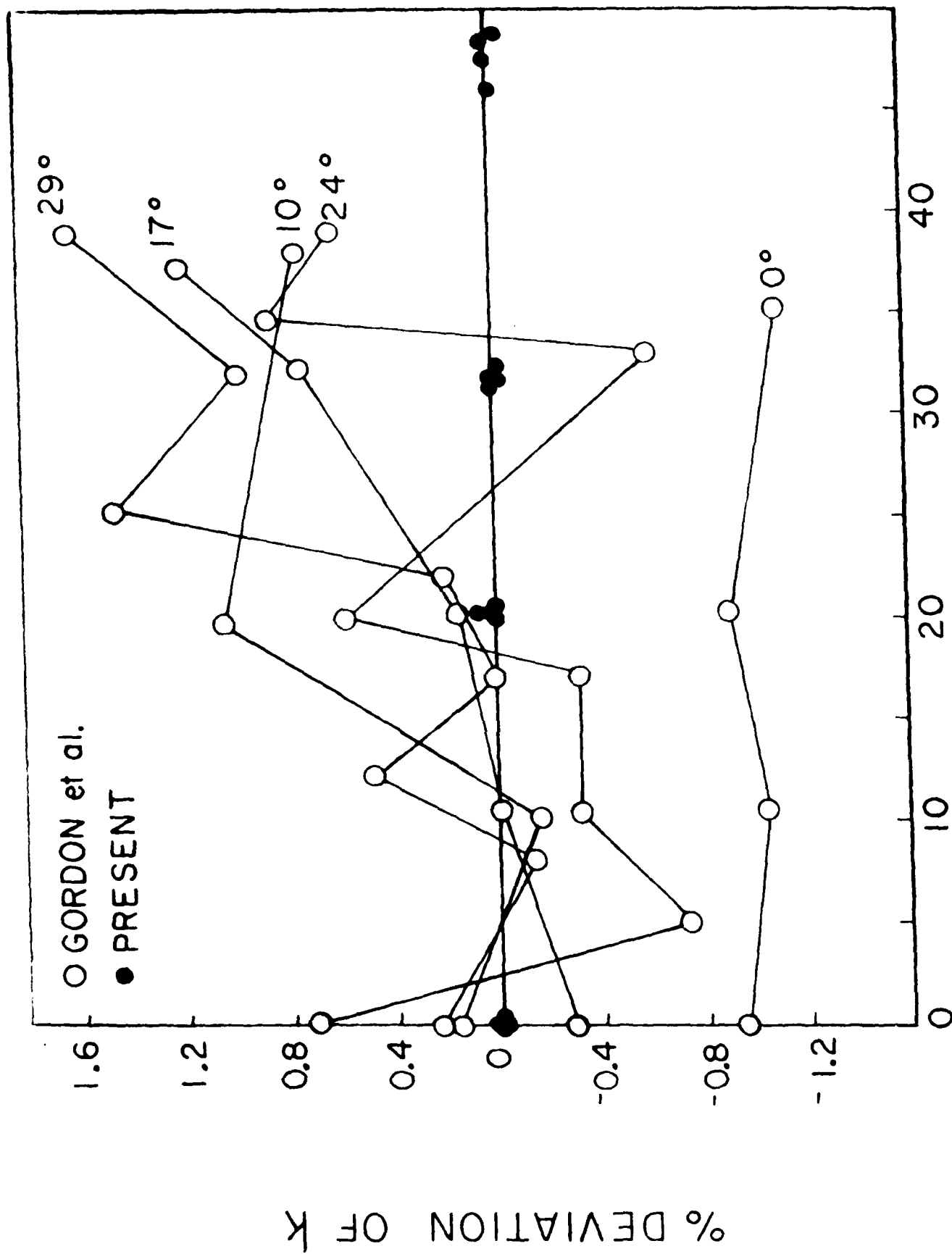
Fig. 4

many more points at zero salinity than those indicated.
The values of Gordon et al. also are shown as a function
of salinity at five temperatures from 0 to 29°C.   In
addition to large fluctuations they exhibit apparent
systematic deviations which depend upon temperature.
Fig. 5 compares the experimental values of both Gordon et
al. and Crozier and Yamamoto with our results for the
temperature variation of the solubility of hydrogen in water
with the 30-40‰ salinity range typical of the oceans.

3. Data accumulation and analysis system.

For very precise isotopic ratio measurements with the
mass spectrometer we have designed and constructed a very con-
venient new system for taking and analyzing the data.   It
incorporates a voltage-to-frequency converter and commercially
available timer, counter, and printer units into an automatic
sample changing system that electronically averages noise
from the difference amplifier in the null balance system.
The system yields superb results.   The precision achieved
with electronic averaging of the noise is both greater and
more objective than with visual averaging.   In addition, the
time for taking and analyzing the data is reduced by approxi-
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□ YAMAMOTO
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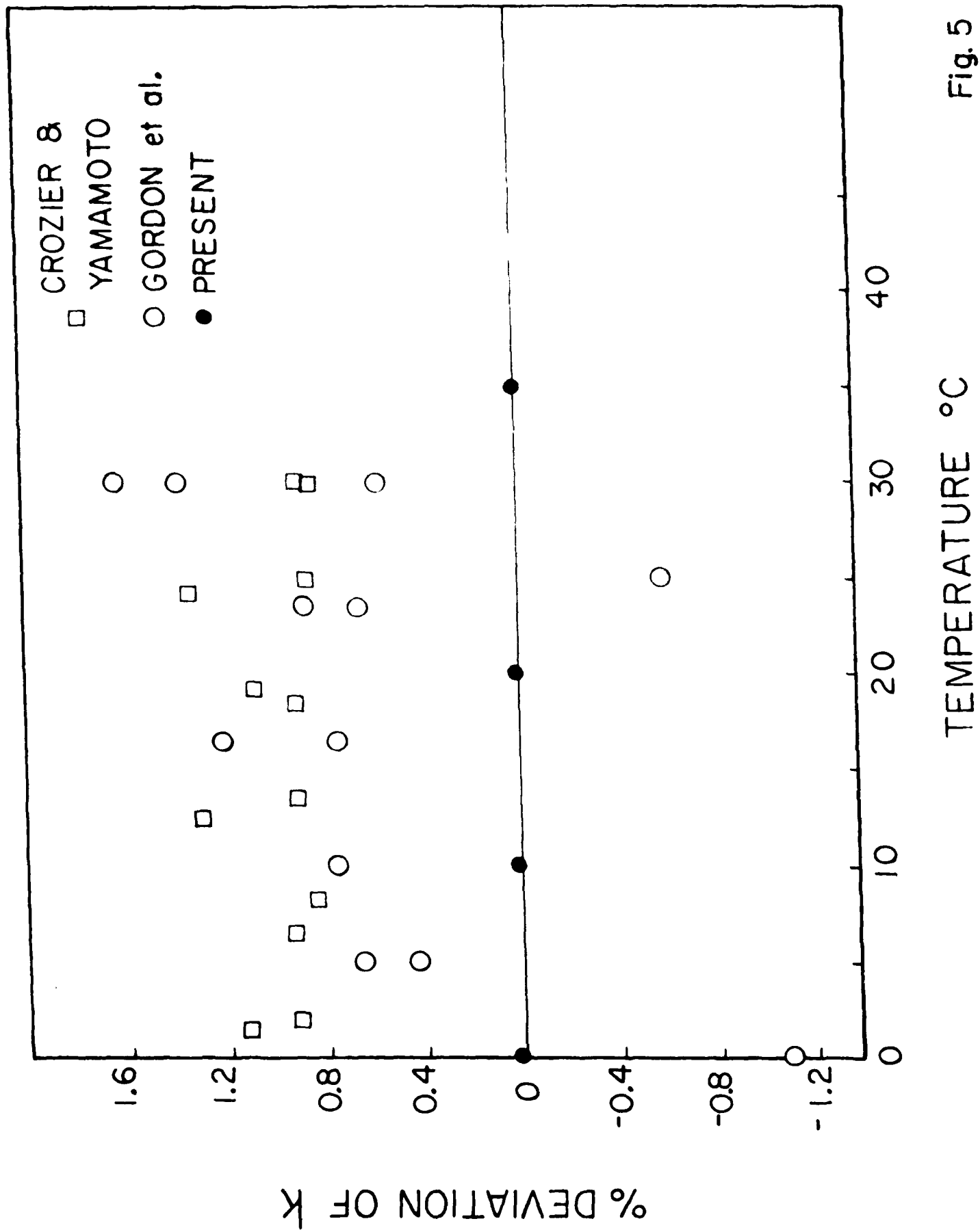
TEMPERATURE °C

% DEVIATION OF K

Fig. 5

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